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Chemically treated membrane filters were evaluated to collect hydrogen sulfide and sulfur dioxide. Four chemical treatments were tested. Silver nitrate and silver nitrate-tartaric acid filters were used to collect hydrogen sulfide, and lithium hydroxide and potassium bicarbonate were used to collect sulfur dioxide. Sampling was performed using a tandem filter holder so that the test gas would pass through each filter in sequence. A pre-filter was used to remove the aerosol component.

For collecting hydrogen sulfide, the silver nitrate filters had an efficiency of 84% when used with a flow rate of 1.0 liter/minute; for collecting sulfur dioxide, the lithium hydroxide filters had an efficiency of 85% at 1.0 liter/minute. It was found that the silver nitrate filters began to absorb sulfur dioxide after several days; thus, the test gas should pass through the lithium hydroxide treated filter prior to the silver nitrate treated filter.

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COLLECTION OF SULFUR GASES WITH CHEMICALLY-TREATED FILTERS

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ABSTRACT

Chemically treated membrane filters were tested for use in collection and measurement of hydrogen sulfide and sulfur dioxide. Four chemical treatments were tested. Silver nitrate and silver nitrate-tartaric acid filters were used for collection of hydrogen sulfide, and lithium hydroxide and potassium bicarbonate were used for collection of sulfur dioxide. Sampling was performed using a tandem filter holder so that the test gas would pass through each filter in sequence. There was a pre-filter whose function was to remove the aerosol component.

For collection of hydrogen sulfide the silver nitrate filters had an efficiency of 84% when used with a flow rate of 1.0 liter/minute, and for collection of sulfur dioxide the lithium hydroxide filters had an efficiency of 85% at 1.0 liter/minute. It was found that the silver nitrate filters began to absorb sulfur dioxide after several days, so the test gas should pass through the lithium hydroxide treated filter prior to the silver nitrate treated filter.

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SECTION 1

INTRODUCTION

A principle source of atmospheric sulfur may be from sulfate reduction by anaerobic bacteria (1,2). One of the significant products of the reduction may be hydrogen sulfide, which could be oxidized and contribute to the atmospheric sulfate loading.

A simple, inexpensive method is needed to measure simultaneously long-time averages of hydrogen sulfide (H_2S), sulfur dioxide (SO_2), and aerosol concentrations. Treated filters offer a method of measuring wide variations of these concentrations, since the flowrate through the filter can be adjusted to yield a collected sample within the sensitivity limits of the analysis method. A tandem filter setup was chosen to prevent contamination of the SO_2 and H_2S adsorbing filters with particulate sulfur.

Sampling of H_2S and SO_2 has been described by Adams (3), Pate et al (4), and Natusch (5) and Huygen (7). Collection methods similar to that discussed here have been described by Ensinger (6) and Lewin et al (9).

SECTION 2

CONCLUSIONS

Lithium hydroxide (LiOH) and potassium bicarbonate ($KHCO_3$) treated filters were compared for their ability to collect SO_2. The LiOH treated filter was found to be better since its collection efficiency remained unchanged for periods of up to a month, and the $KHCO_3$ treated filters lost efficiency and selectivity after one day. The efficiency of the LiOH treated filters dropped sharply at humidities less than 30%.

Silver nitrate ($AgNO_3$) and silver nitrate-tartaric acid ($AgNO_3$-tartaric acid) treated filters were used to collect H_2S. Their efficiencies were shown to be dependent on humidity.

A flow rate of 1.0 liter/minute appeared to be best for short sampling times and high efficiency. The best filter sequence was found to be; (1) Teflon prefilter, (2) LiOH treated filter, and (3) $AgNO_3$ treated filter. Under these conditions efficiencies of about 84% and 85% can be expected from the $AgNO_3$ and LiOH filters for H_2S and SO_2, respectively, when analyzed by X-ray fluorescence.

SECTION 3

EXPERIMENTAL PROCEDURES

GENERATION OF TEST GAS

In Figure 1 is shown the system used to test the chemically treated filters. The test gas consisted of zero air (less than 1 ppm hydrocarbon), humidified zero air, and one or more sulfur containing gases (given off by a permeation tube). All of the elements of the test gas were combined and the total flow, humidity, and temperature were determined.

For the compounds tested, a permeation tube in a constant temperature bath was used to generate the test mixture. The permeation tube was housed in a glass or Teflon chamber in series with metal heat-transfer coils. The temperature bath was regulated to within $\pm$ 0.1°C. (For almost all test runs the temperature bath was set at 20 $\pm$ 0.1°C.)

Zero grade air was further cleansed by passing the air through activated charcoal and a drying agent. The flow was adjusted using a needle value and a Brooks rotometer (Model I355-00AIIAAA). Before being run through the test filters, additional zero air and/or humidified zero air was often added to the test gas mixture to adjust the humidity and total flow rate. The humidity of the test gas was then measured by an EG&G Model 880 dewpoint hygrometer. Teflon tubing and stainless steel connectors were used to minimize any reactivity of the test gases with the laboratory apparatus.

MEASUREMENT OF TEST GAS CONCENTRATION

After the test gas mixture had stabilized, its concentration was measured with a Meloy model SA-160-2 sulfur gas analyzer. The analyzer was previously calibrated using known sulfur containing gas concentrations.

The sulfur analyzer output voltage was displayed on a digital voltmeter (DVM), which was recorded after the voltage transients due to concentration

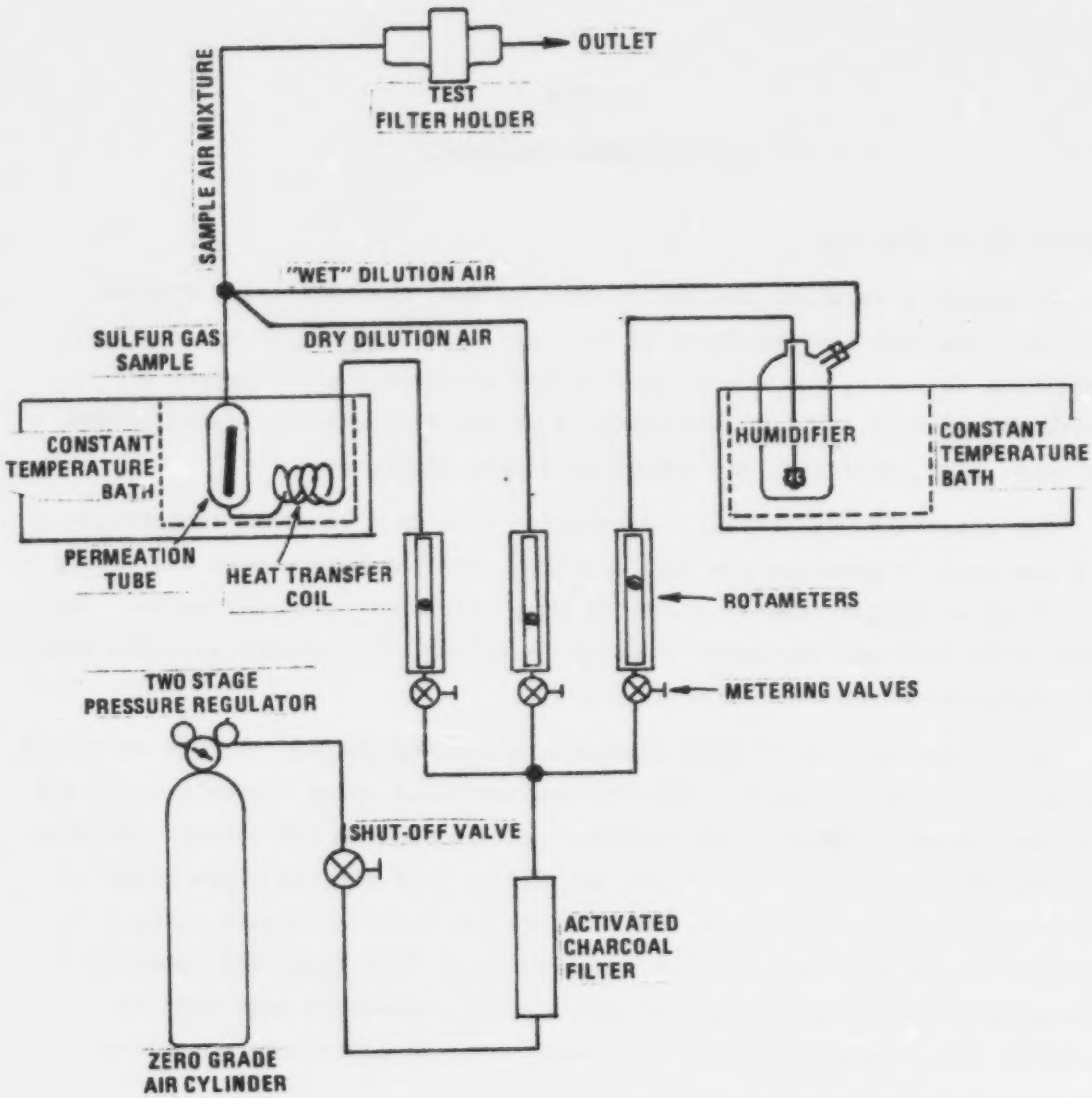

Figure 1. Laboratory sampling unit.

fluctuations disappeared. After recording the voltage, the analyzer was disconnected from the test gas line and the filter holder was placed in series between the test gas generator and the sulfur gas analyzer. The analyzer measured the sulfur gas concentration of the test gas that passed through the filter, and readings were recorded a few minutes before the end of the test run. Test runs usually lasted 60 minutes. If the analyzer's output voltage for the filter run was the same as the voltage for the lab air, it was assumed that the filter collected 100% of the sulfur gas.

FILTER HOLDERS

In Figure 2 is shown the three-element filter holder. The filter holder consists of a modified Millipore single filter holder No. XX-50-04700, which has been elongated and is fitted with three stainless steel discs to separate the three filter elements. Teflon or Vitron rings are used to seal the filter elements in the holder.

This tandem filter holder was developed to prevent the filters from touching. It was found that filters which touched produced erroneous results.

FILTER PREPARATION

A number of cellulose filter types were tested, and the Millipore WSWP04700 filter paper was chosen because of its combination of strength, thinness, and surface structure.

This inexpensive filter was treated in chemical solutions to make selective collectors for the various volatile sulfur compounds found in the atmosphere. The two sulfur compounds of primary interest were SO_2 and H_2S. Adams (3), Pate el al (4), Natusch and Hinygen (5) listed many different chemical solutions that absorb SO_2 and H_2S. Several of these solutions were chosen and tested. For SO_2, lithium hydroxide (LiOH) and potassium bicarbonate ($KHCO_3$) were tested. For H_2S, silver nitrate ($AgNO_3$) described by Ensinger (6) and silver nitrate-tartaric acid ($AgNO_3$-tartaric acid) were tested.

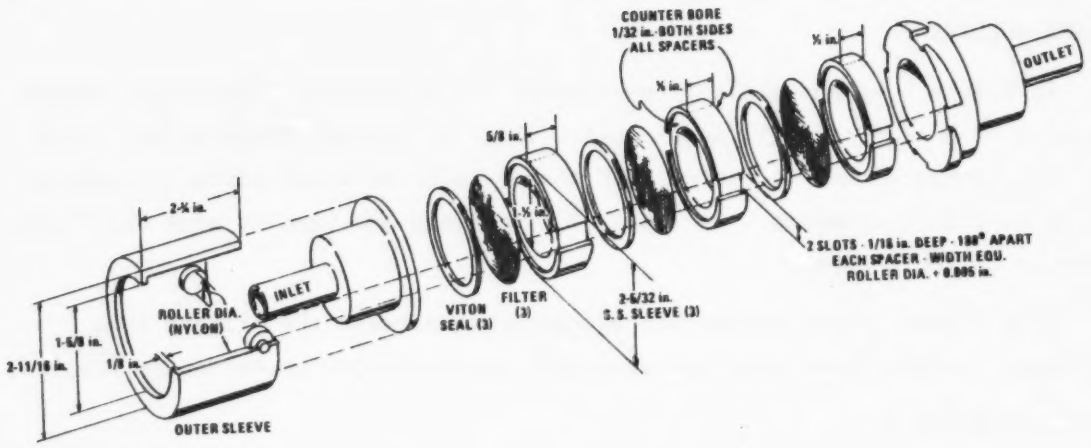

Figure 2. Three element filter holder.

SO_2 FILTER-LiOH SOLUTION

Solution:

36g LiOH
20 ml 9% triton-x-305
30 ml propylene glycol
dilute to 1000 ml with deionized water

pH 11.63

Blank Millipore WSWP04700 filters were treated as follows: The filters were soaked in the solution for 6-7 minutes. After soaking, the filters were placed on a glass plate and the excess solution was carefully squeezed out by rolling with a glass test tube. The filters were then dried by hanging in ambient air for at least one hour (the room must be low in volatile sulfur compounds and of low or moderate humidity). After drying the filters were stored in Millipore petrislides at ambient temperature until used.

SO_2 FILTER-$KHCO_3$ SOLUTION

Solution:

10g $KHCO_3$
7.5 ml glycerine
dilute to 50 ml with deionized water

pH 8.34

In preparing filters treated with $KHCO_3$, a special problem was encountered. The $KHCO_3$ is reduced easily to form a compound which is not selectively reactive with SO_2. To achieve the best possible results several methods of filter preparation were used, and the resulting filters were tested.

The methods are as follows:

1. A 0.2 ml aliquot of the solution was applied to the center of the filter and was allowed to spread evenly throughout the filter.
2. A 1.0 ml drop of solution was deposited in the center of the filter and was allowed to spread evenly through the filter.
3. A pump sprayer was used to deposit 3.0 ml of solution evenly on the filter.

4. The filter was dipped into the solution for 1 second, removed and allowed to dry for 1 hour.

Method #3 had the best efficiency for the collection of SO_2 and showed the longest lifetime. It was adopted as the method of production for $KHCO_3$ filters.

H_2S FILTER-$AgNO_3$ SOLUTION

Solution:

15g $AgNO_3$
25 ml propylene glycol
dilute to 290 ml with deionized water

pH 3.12

Filter preparation for the $AgNO_3$ soaked filters was exactly the same as for LiOH soaked filters, except that the filters were soaked for 20 minutes in the solution. These filters must be stored in darkness until used.

H_2S FILTER-$AgNO_3$-TARTARIC ACID SOLUTION

Solution:

2g $AgNO_3$
4.5g tartaric acid
3 ml propylene glycol
dilute to 100 ml with deionized water

pH 2.0

Blank WSWP04700 filters were treated as follows: The filters were soaked in solution for 30 seconds, placed between two Gelman type AE high volume filters, and dried in a oven at 75°C for 1 hour. After drying, the filters were placed in individual Millipore petrislides and stored in darkness at ambient temperature.

TEST PROCEDURES

The filter was removed from the petrislide using tweezers and positioned in the filter holder, so that the chemically treated side of the filter faces the incoming air flow. The type of filter holder used, single or tandem, is dependent on the type of test to be done. Some of the tests involved using a prefilter, SO_2, and H_2S filters, while others were carried out on only one

filter. Some of the different tests had variables such as flow rate, humidity, temperature, wetting of the prefilter, and filters in contact with each other.

FIELD WORK

During field tests, a central location was established. At this location the loading of the filter holders was carried out and all record keeping was done.

The order of the filters was established to be an aerosol prefilter, and SO_2 filter, and an H_2S filter. The SO_2 filter was made from the LiOH solution and the H_2S filter was made from the $AgNO_3$ solution.

A complete monitoring station consisted of a three element filter holder and a vacuum source.

DESCRIPTION OF VACUUM SOURCE

The Vacuum source (Figure 3) is a Gast #1531 vane type 0.1 hp vacuum pump mounted in a metal box. An aluminum bracket is attached to one end of the box and a control valve and two female bulkheads terminated by hose connectors are mounted on the bracket. The vacuum pump is cooled during operation by a ventilation fan. The complete assembly weights 8.6 kg. (19 lbs.) and draws 1.5 amperes from a 115 volt power line.

To maintain constant flow, a Millipore critical orifice (1 liter/ minute) is screwed into the outlet of the filter holder. The outlet part of the filter holder is connected to the hose connectors of the vacuum source with 6.3 mm (0.25 in.) rubber tubing. If only one holder is used, one of the hose connectors must be capped.

To operate correctly, the vacuum at the critical orifice must be greater than the critical vacuum specified. (Beyond the critical vacuum, flow through the orifice will be constant.) The control valve in the box allows the pump to be loaded past critical vacuum while providing enough air to prevent pump overheating.

FILTER ANALYSIS

At the end of the test run or field run the filters were returned to the petrislides and submitted for analysis. The two methods of analysis

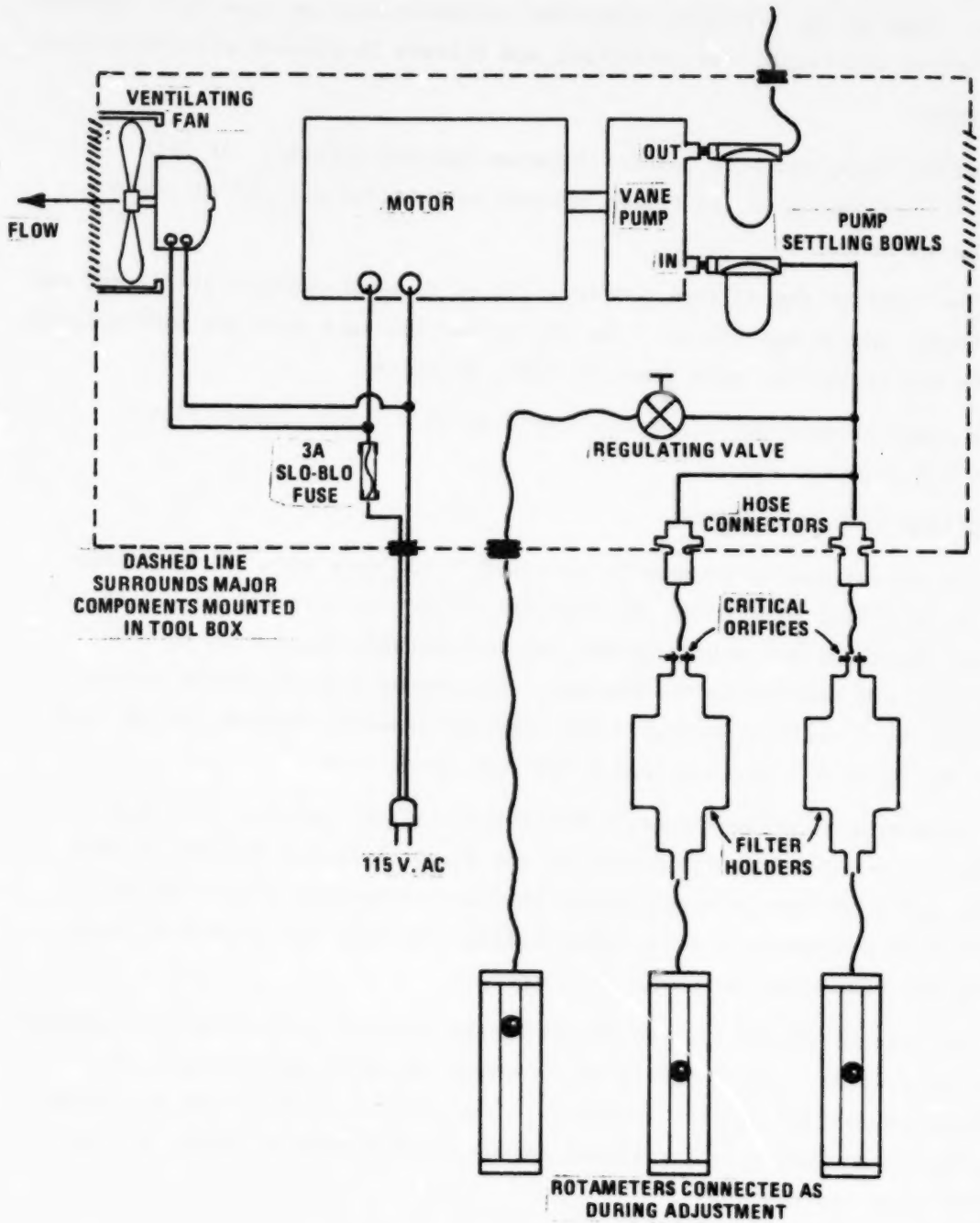

Figure 3. Vacuum source.

used were: (1) an energy-dispersive X-ray fluorescence analyzer for sulfur density at the surface of the filter and (2) liquid ion chromatography for sulfate.

SECTION 4

RESULTS AND DISCUSSION

PREFILTER

An untreated 47 mm filter is used in front of the selectively reactive filters to collect the aerosol content of the sample gas. It is important that the prefilter be unreactive to the sulfur containing gases in the sample and that it not restrict flow. The prefilter also creates turbulence and insures an even distribution of sample on the selectively reactive filters following the prefilter. The first experiments were carried out using a Millipore WSWP04700 as the prefilter. However, pH measurements on these filters revealed that it is slightly alkaline. It is possible that the acidic H_2S may be adsorbed in small amounts by this prefilter and that a better choice of prefilters could be made.

Testing showed that the Millipore FALP04700, a Teflon filter (1.0 μm pore size) was very close to being neutral. This filter caused no noticeable restriction of flow in our field setup, yet gave a more even distribution of sample on the succeeding sulfur gas filters.

FILTER TEST RESULTS

The collection efficiency in SC/SEX100%, where SE is the amount of sulfur containing gas molecules entering the filter and SC is the amount collected. SE is controlled using a permeation tube of known permeation rate. The efficiency of H_2S and SO_2 collection was found to be a function of both humidity and flow rate for the $AgNO_3$ and LiOH filters. In all of the cases sited below, XRF was used to determine the efficiencies. The Meloy sulfur gas analyzer indicated 100% efficiency during all of these runs. The efficiencies of less than 100% were attributed to adsorption beneath the surface of the filter. Most likely, the difference in efficiencies measured by the Meloy sulfur analyzer and by XRF was not due to a

loss of adsorbed sulfur by the filter, since repeated analysis of the filters gave nearly identical results.

FLOW RATES

The efficiencies of the $AgNO_3$ and LiOH filters were tested over a range of 0.5-2.0 liter/minute. The results of these runs are given in Tables 1 and 2. For $AgNO_3$ filters run using a prefilter the flows of 0.5 liter/minute and 1.0 liter/minute gave mean efficiencies of 84.6% (std. dev. = 5.55) and 84.3% (std. dev. = 6.52) respectively. The LiOH filters run with a prefilter showed an optimum flow rate of 1.0 liter/minute with an efficiency of 84.6% (std. dev. = 4.13).

HUMIDITY

At each of the flow rates the relative humidity of the test gas was varied from 10% to 100% (when possible). The results of these runs are given in Tables 1 and 2. As noted before the LiOH filters at 1 liter/minute had a mean efficiency of 84.6% (std. dev. = 4.13) and the $AgNO_3$ at the same flow rate had an efficiency of 84.3% (std. dev. = 6.52). It was noted that the efficiency of the LiOH dropped sharply at relative humidities less than 39% which has been reported in the past by Lewin and Zacheu-Christensen (9) when using alkaline impregnated filters to collect SO_2.

TEMPERATURE

A cursory test of temperature effects on the treated filter efficiency was carried out. No efficiency changes were noted in the range of 10-30°C for both LiOH and $AgNO_3$.

SATURATION TIMES

The Meloy sulfur analyzer with a strip chart recorder was used to monitor relative efficiencies of the filters over long periods of time. The four types of treated filters were run over night to determine the saturation limit of each. The saturation limits are given in Table 3 where the time is the duration that the filter exhibited 100% efficiency. For samples of this magnitude X-ray fluorescence cannot be used since there is a great deal of sample penetration. This was shown by doing XRF on the exposed filters on both sides. Nearly equal quantities of sulfur were

TABLE 1. EFFICIENCIES OF $AgNO_3$ TREATED FILTERS
(EXPECTED SULFUR DENSITY-1.12 $\mu g/cm^2$)

Flow (1/min)		Relative Humidity										Efficiency	
		10%	20%	30%	40%	50%	60%	70%	80%	90%	100%	Mean	Std. Dev.
0.5	S detected, $\mu g/cm^2$:		0.95	1.00	0.93	1.05	1.00	0.95	0.90	0.90	0.85	84.6	5.55
	Efficiency, %:		85	89	83	94	89	85	80	80	76		
1.0	S detected, $\mu g/cm^2$:	0.90	0.88	0.90	0.90	1.01	1.10	0.91	0.98	0.94		84.3	6.52
	Efficiency, %:	80	78	80	80	90	98	81	88	84			
1.5	S detected, $\mu g/cm^2$:	0.92	0.82	0.94	1.02	1.00	0.96	0.95	0.84			83.1	6.31
	Efficiency, %:	83	73	84	91	89	86	85	75				
2.0	S detected, $\mu g/cm^2$:	0.92	0.83	0.98	0.83	0.92	0.92	0.84	0.92			79.9	5.03
	Efficiency, %:	82	74	88	74	82	82	75	82				

TABLE 2. EFFICIENCIES OF LiOH TREATED FILTERS
(EXPECTED SULFUR DENSITY-0.62 μg/cm^2)

Flow (l/min)		Relative Humidity										Efficiency	
		10%	20%	30%	40%	50%	60%	70%	80%	90%	100%	Mean	Std. Dev.
0.5	S detected, μg/cm^2:	0.13	0.35	0.40	0.43	0.42	0.45	0.44	0.45	0.44	0.47	69.1	5.86
	Efficiency, %:	21	56	65	69	68	73	71	73	71	76		
1.0	S detected, μg/cm^2:	0.30	0.50	0.52	0.53	0.51	0.55	0.53	0.55	0.55	0.48	84.6	4.13
	Efficiency, %:	48	81	84	85	82	89	85	89	89	77		
1.5	S detected, μg/cm^2:	0.14	0.09	0.22	0.45	0.43	0.45	0.46	0.39	0.46		71.0	4.20
	Efficiency, %:	22	14	35	73	70	73	74	63	74			
2.0	S detected, μg/cm^2:	0.13	0.17	0.15	0.20	0.28	0.28	0.29	0.32			47.2	3.30
	Efficiency, %:	21	27	24	32	45	45	47	52				

found on each side of the exposed filters. Ion chromatograph would be a preferable measure of exposures of this intensity.

TABLE 3. SATURATION LIMITS FOR EACH FILTER TYPE

Filter type	LiOH	$KHCO_3$	$AgNO_3$	$AgNO_3$/ tartaric acid
Sulfur gas	SO_2	SO_2	H_2S	H_2S
Time (hours)	4.5	7.0	24	18
Concentration (PPB)	119	119	63	63

SELECTIVITY

All four treated filter types are 100% selective to their respective sulfur gases when they are freshly made. That is, $KHCO_3$ and LiOH treated filters do adsorb H_2S and $AgNO_3$ and $AgNO_3$ tartaric acid treated filters do not adsorb SO_2. However only the LiOH filter has a selectivity lifetime greater than one month. The $AgNO_3$ filter begins to pick up small amounts of SO_2 after approximately 2 days. The $KHCO_3$ treated filters will pick up both H_2S and SO_2 after they are a day old, unless they are refrigerated. Tests of selectivity lifetime have not been performed on the $AgNO_3$-tartaric acid treated filters, but is appears to be very much the same as for $AgNO_3$. Because of the eventual loss of selectivity in the $AgNO_3$ filters, it was decided that the test gas flow should go through the prefilter first, then the LiOH filter, with the $AgNO_3$ filter being last.

Other sulfur compounds were used to further test the selectivity of the LiOH and $AgNO_3$ filters. The results of these tests are summarized in Table 4.

TABLE 4. INTERFERENCES FROM OTHER ORGANIC SULFUR COMPOUNDS ON EACH FILTER TYPE

GAS	FILTER TYPE	
	LiOH	$AgNO_3$
H_2S	N	G
SO_2	G	N
CH_3SH	N	N
$(CH_3)_2S$	N	N
$(CH_3)_2S_2$	N	N
CS	N	N
COS	N	N

G = Good Collection
N = No Collection

DETECTION TECHNIQUES

The Meloy sulfur gas analyzer (model SA-160-2) served as a good in situ guide to the effectiveness of the filter being exposed. Using the predetermined calibration curve, the concentration of the test gas (SO_2 or H_2S) could be determined both before and after passing through the filter.

Filter analysis was done by two means. X-ray fluorescence, described by Lorenzen (6), was used the majority of the time. A newer technique, ion chromatography using the Dionex Model 14 ion chromatograph, is presently being examined.

The X-ray fluorescence method (XRF) measures only surface deposition. This was found not to be a limitation except for exposures when a significant amount of sample was adsorbed beneath the surface of the filter. The center-weighted reading of the XRF posed some problems since the deposition on the filter was also center-weighted. The results of the XRF were consistent enough, however, that this could be taken into account when

calculating concentration. Advantages of the XRF are that analysis can be done relatively quickly and it leaves the filter intact for further tests.

The ion chromatograph (IC) has the advantage that it can measure the total sulfur present with no concern for the distribution of deposition. However, the results from the IC to date have been too inconsistent to make any quantitative statements on the method.

MINIMUM DETECTION LIMIT

The concentration of sample is related to the density of sulfur detected using the equation:

$$\text{Concentration, ppb} = \frac{\text{volume of sulfur containing molecules} \times 10^9}{\text{volume of air}}$$

$$= \frac{DA}{EFt} \times \frac{(24.6\ 1/\text{g mole air})\ (10^{-6}\ \text{g}/\mu\text{g})\ (10^9)}{(34.08\ \text{g S/g mole S})}$$

where D is the sulfur detected by X-ray fluorescence and has the units $\mu g/cm^2$, E is the fractional collection efficiency, F is the sample volumetric flow rate in liters/min, t is the sampling time in minutes, and A is the area of collection. The quantity 24.6 1/g mole is the molar volume of an ideal gas at 25°C and 1 atm. This equation holds for a sample containing 1 atom sulfur per molecule. The fractional collection efficiencies for $AgNO_3$ and LiOH filters were approximately 0.865, flow rate is usually 1.0 1/min, and the minimum detectable density by X-ray is 0.05 $\mu g/cm^2$. The actual area of the filter is 8.04 cm^2. Reducing the above equation, the minimum detectable concentration becomes simply a function of sample time:

$$\text{Minimum concentration (ppb)} = \frac{335}{t} \text{ where t is in minutes.}$$

Sample Time (minutes)	Minimum Concentration (ppb)
30	11.17
60	5.58
120	2.79
240	1.40
360	0.93
720	0.46

DEPOSITION OF SAMPLE

It was desired to have the sample deposited only at the surface of the filter so that accurate analysis could be accomplished using X-ray fluorescence. With the particulate filters there was no apparent adsorption of the sample below the filter surface for any of the filter types tested. For the selectively reactive filters no penetration was found for exposures corresponding to roughly 50% of the saturation limit. It was also found that for sampling rates greater than 2.0 liters/minute that some penetration was found for LiOH.

Due to the design of the filter holders, the deposition of sample on the filter was not radially uniform. The local velocity of the sample gas at the edge of the filter was lower than the local velocity at the center of the filter. The resulting "center-weighted" deposition was analyzed using an X-ray beam which looks mainly at the center of the filter. This gave readings higher than the actual average surface density of the sample. It was reasoned that as long as the surface deposition distribution had the same shape for each run, that the results would be consistent. No efficiencies of 100% or greater have been seen in the laboratory tests using a profilter so the "center-weighted problem" should not be resulting in any exaggerated field measurements.

X-ray analysis had continually indicated that the selective filters run without particulate were more efficient than those run with particulates. Yet, tests on the prefilters indicated that they were not adsorbing the sample. In reality, the presence of the prefilter increased the turbulence behind it. By increasing the turbulence, the velocity of the center of all successive filters was more nearly equal the velocity at the edge, i.e. the deposition was less "center-weighted." The density of the filters run with prefilters would then appear to be less than those run without them.

The deposition on the particulate filter is center-weighted and there is no way to modify this without redesigning the filter holder. However, it is felt from comparisons of readings from alternative aerosol measuring

devices that the accuracy of the X-ray technique on particulates run in these holders is very good.

WETTING

Tests were run to determine the consequence of a WSWP prefilter becoming wet during a normal run. One drop of deionized water was placed on the prefilter and it was exposed to a sulfur gas. Wet prefilters picked up about 0.11 μg of SO_2. No adsorption of H_2S by the wet prefilter was indicated by XRF.

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